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CHEMICAL & ENGINEERING

NEWS

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DETERGENTS

Components grow more diverse and complex

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CHEMICAL & ENGINEERING
NEWS
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JANUARY 25, 1988

News of the Week

■ **Sterling Drug adopts defense tactics to fight off would-be acquirer Hoffmann-LaRoche, the Swiss-based pharmaceutical firm.** **Page 4**

■ **A. H. Robins accepts American Home Products bid, reversing earlier decision to accept offer from French pharmaceutical firm Sanofi.** **Page 4**

■ **Superconducting Super Collider project may face significant federal budget problems in future.** **Page 5**

■ **Massachusetts Institute of Technology will phase out its department of applied biological sciences over the next year and a half to the dismay of its faculty and alumni.** **Page 6**

■ **Prominent U.S. and Soviet chemists take lead role in call for comprehensive treaty that would ban all nuclear weapons tests.** **Page 6**

Cover: BASF research chemist works with Terg-O-Tometer to evaluate experimental laundry detergent formulations

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Business

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Olin's earnings increase markedly in 1987, mostly as a result of ongoing restructuring program begun in 1985. **Page 12**

Government

EPA's proposed new regulations reflect comprehensive effort to protect health of all workers handling commercial pesticides. **Page 14**

NIH's recombinant DNA guidelines adjudged not violated by Montana professor's controversial inoculation of elm trees. **Page 15**

Science

U.S. scientists' human rights committees publicly protest continued unjust imprisonment of 13 Somalian scientists. **Page 17**

First sonoluminescence spectra obtained from hydrocarbon and halocarbon liquids by University of Illinois chemists. **Page 18**

Technology

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Books

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Product Report

Detergent makeup grows increasingly diverse and complex as producers tailor products to suit needs of both household and industrial customers. **Page 21**

Chemical & Engineering News

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LETTERS

Canadian compromise

SIR: I have participated in the discussions concerning the alternative American and European labelings of the groups in the periodic table. It appears that our efforts are likely to produce yet another recommendation whose sole virtue is that it is equally offensive to both sides.

I would like to propose a typically Canadian compromise: The rest of the world should adopt the American (ABA) labeling of the periodic table. In return, Americans will agree to spell correctly sulphur, caesium, aluminium, metre, and litre.

John S. Martin
University of Alberta, Edmonton

Women in science

SIR: My appreciation to C. Schuerch for his letter on minorities in science (C&EN, Nov. 9, 1987, page 46). It is an excellent example of how those in the majority rationalize discrimination. The fact that it exists now and can be explained, fallaciously or otherwise, does not make it any less real or tolerable.

At the risk of crossing the same line, I wish to also comment on the same Editorial, "Women, minorities, and chemistry" (C&EN, Sept. 14, 1987, page 3). It was pointed out that though "women still have no more than a toehold in graduate chemistry faculties, . . . chemistry is making tangible progress" as evidenced by the increase in the number of women earning degrees in chemistry. To me this is not evidence of progress, but of an increasing problem. The universities have been willing to take our money and benefit from our cheap labor for quite a while. It is no surprise that university programs to increase enrollments and budgets are resulting in more women undergraduate and graduate students. But, as the statistics indicate, this only increases the number of women not being hired.

Until minorities are welcomed into the faculty ranks, chemistry will remain one of the "culprits," as Erich Bloch stated.

Debra L. Mellish
Absecon, N.J.

Employment outlook

SIR: In "1988 Employment Outlook" (C&EN, Oct. 26, 1987, page 33), Bette Hileman lists falling undergraduate and graduate enrollments as problems for chemical education and reports on various proposals to address these "problems" (page 35). Yet, on page 49 we have, "A number of the new Ph.D.s are still looking for work, or else have taken postdoctoral positions only because they have failed to locate jobs in industry." Still worse, page 57 has, "If they are adjusted for inflation, salaries for chemists at all three degree levels either were unchanged or declined. The lack of change in Ph.D.s' salaries is unprecedented in the 20 years that ACS has made annual surveys of members' salaries."

With regard to problems in chemical education, my nomination for the most serious problem is that people are spending five or six years getting a Ph.D. in chemistry and then discovering that they do not have marketable skills. With regard to salaries, I point out that companies do not normally bid up the price of goods and services that are in constant oversupply. What is surprising is not that salaries are stagnant but that they have not already been stagnant for years. The cause of these situations is clear: We have too many chemistry graduates in general and too many chemistry Ph.D.s in particular.

The suggestion, discussed elsewhere in Hileman's report, to reduce the number of Ph.D.-granting institutions is a good one. ACS president Mary Good's argument to the contrary simply does not wash. She suggests that "departments ought to focus only on areas in which they can be front-runners," but with 225 institutions competing it is clear that many will be unable to be front-runners in any area.

The students may, in any case, render this point moot. Back on page 35 we also have, "The number of Ph.D.s will almost inevitably decline during the next decade or so because the pool of undergraduate majors is smaller." I see this development as a very positive one for the profession. The oversupply of Ph.D. chemists I spoke of has existed, albeit in varying degrees of severity, for at least 20 years. Could it be that supply will finally adjust to demand?

Gordon G. Cash
Southbury, Conn.

Air pollution control

SIR: I read with interest the article, "Rhine Recovers from Last Year's Sandoz Chemical Spill" (C&EN, Nov. 9, 1987, page 16). It is particularly interesting since I was at Ciba-Geigy and at BASF, Ludwigshafen, during the period Oct. 27 through Nov. 5. At BASF I had a meeting with their engineering staff in

Glasses are examined for traces of spotting and filming from dishwashing detergent at BASF lab in Wyandotte, Mich.

Detergent Components Become Increasingly Diverse, Complex

Bruce F. Greek, C&EN Houston

The demands of the marketplace make surfactants an ever-changing business as the needs of both household and industrial customers force producers to tailor their products.

Extensive research and development by surfactant producers and detergent formulators has broadened the uses of surface active agents. Materials in detergents and other cleaners have become ever more diverse and complex as producers move to meet stringent demands of consumers.

A wide variety of cleaners and other products having surface active properties currently are used by household and industrial/institutional consumers. But growth in demand for surfactants will slow in 1988 and remain only slightly above the average growth rate of the previous decade or so. Markets for detergents and other surfactant products already are greatly fractionated and probably will become even more so as consumers take to new products when they hit the marketplace.

Surfactants occupy a large segment of the chemical industry, and marketing success of this segment stems from the very heterogeneity of the products containing surfactant materials. No one formulation, detergent, or surfactant fits every use. Inventory of cleaning materials in a typical household might include half a dozen or more formulated products designed to be the most suitable for a specific job, whether cleaning clothes, floors, or automobiles.

In industrial and institutional markets, many surfactant materials find their way to more than just cleaning jobs. For example, they are widely used to separate oil from water in enhanced oil recovery. They also are used in making emulsions of tar and water for quick application and for subsequent demul-

Makeup of powdered heavy-duty laundry detergents

Functional agent	Typical materials	Range of use, %
Surfactant	Alkylbenzene sulfonates	0 to 20%
(anionic/cationic/nonionic)	Fatty alcohol ether sulfates	0 to 15
	Alkyl or nonylphenol polyethylene glycol ethers	0 to 15
Builders (chelating agents)	Sodium tripolyphosphate	0 to 50
Ion exchangers	Zeolites, polyacrylic acids and derivatives	0 to 50
Alkalies	Sodium carbonate	0 to 35
Bleaches	Sodium perborate/percarbonates	0 to 5
Fabric softeners	Quaternary ammonium salts	0 to 5
	Clays	0 to 5
Anticorrosion materials	Sodium silicate	0 to 25
Antiredeposition materials	Cellulose ethers	0 to 0.5
Enzymes	Proteases, amylases	0 to 2
Optical brighteners	Stilbene derivatives	0 to 0.25
Fragrances, dyes	—	0 to tiny
Fillers	Sodium sulfate	Balance

sion to bind the tar to gravel in building roads. The industrial and institutional markets also are changing, possibly more rapidly than the household markets, as industry changes its processing and manufacturing methods.

Because the end products of detergent materials are diverse and frequently overlapping, clear-cut definitions of the markets are elusive. It's estimated that more than half the consumption of the materials is by industrial and institutional users (50 to 60%), and more than another quarter goes into household cleaning products (25 to 30%). The remainder goes into personal care products such as cosmetics, shampoos, and toilet soap.

Consumption of detergent materials is difficult to estimate because the formulations are so varied. Household laundry detergents (the largest segment in household consumption) have compositions that include surfactants (the surface active agent itself), builders (chelating agents), bleaches, and numerous additives, all designed to meet the many objectives for which a detergent can be used. The volume of all the kinds of materials that become part of the products that have surface active properties now probably ranges from 25 million to 50 billion lb. This includes active and inert ingredients.

Production and sales data on all kinds of the surfactants alone are available, whether used in cleaning agents or other applications. In 1986, the latest year for which complete data are available, U.S. production of surfactants totaled almost 5.9 billion lb, according to the U.S. International Trade Commission (ITC). That output is 35% more than the 4.37 billion lb reported by ITC for 1982. It also is almost 10% more than production in 1985.

In 1982, however, production fell 14% from about 5.1 billion lb the year before, which reflected the effect of that year's recession. Recovery from the recession slowed in 1985 with a small decline in production that resulted partly from reformulation of many household laundry products, which, in turn, reduced surfactant demand. Allowing for variations due to the economic and formulation factors involved, the average annual growth in production of surfactants during the 1980s has been less than 3%. Because the base is so large, the 3% growth amounts to well over 150 million lb a year. Counting other materials sold with the surfactants in formulated products, the volume addition totals several times that of the surfactants.

Surfactants production last year grew about 4% from 1986. That relatively strong growth was a result of an upbeat economy most of the year and of new product development by surfactant manufacturers and by detergent formulators and marketers. The outlook for 1988 is not as bright because fewer new products are expected to be added as a consolidation of last year's introductions goes on. Surfactants production this year likely will poke along in the 2 to 3% growth range, assuming the general economy holds up.

The immense diversity in production of surfactants also is reflected in ITC data. In 1986, production and/or sales of about 1200 different chemical compounds or groups of compounds as surface active agents were reported. About 170 different companies are represented in the reports. No one compound or compound group exceeded 1 billion lb of production. More than 62% of the production in 1986 was of anionic surfactants, almost 29% was nonionic, and less than 9% was cationic. A small quantity—27.3 million lb—of amphoteric surfactants was reported, or less than 0.5% of total production.

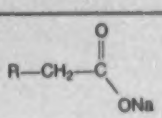
The 1986 surfactants sales reported to ITC totaled more than 3.5 billion lb, with a total value of more than $1.6 billion. The average unit value was 45 cents per lb. In 1985, sales of surfactants exceeded 3.3 billion lb, valued at nearly $1.6 billion, and having an average unit value of 47 cents per lb. Not surprisingly, the low-volume amphoteric surfactants in 1986 had the highest unit value at $1.07. The workhorse anionic surfactants averaged 30 cents per lb, the cationics nearly $1.00 per lb, and the nonionics averaged 50 cents per lb.

Merchant suppliers of surfactants account for more than 60% of production. That group includes most of the large chemical companies and many small specialty producers. The large formulators of detergents—Church & Dwight, Colgate-Palmolive, Lever Brothers, and Procter & Gamble, as well as numerous smaller specialty and private label formulators—also make some of their surfactants. The latter group of producers may sell part of their production to other formulators. Many other companies also produce the basic ingredients of surfactants. Some make ethylene, propylene, and benzene, which are key petrochemical raw materials of surfac-

Surfactants fall into four major chemical groups

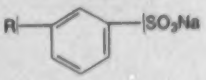
ANIONICS

Carboxylates (soaps)



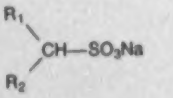
$R = C_{10-16}$

Alkylbenzene sulfonates



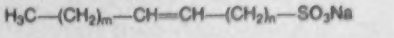
$R = C_{10-13}$

Alkane sulfonates



$R_1 + R_2 = C_{11-17}$

α-Olefin sulfonates

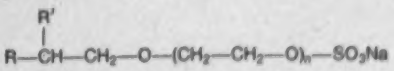


$n + m = 9-15$

Fatty alcohol sulfates

$R = C_{11-17}$

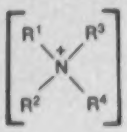
Oxo-alcohol ether sulfates



$R + R' = C_{11-13}$
$n = 1-4$

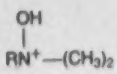
CATIONICS

Quaternary ammonium salts (quats)



$R^1, R^2 = C_{16-18}$
$R^3, R^4 = C_1$

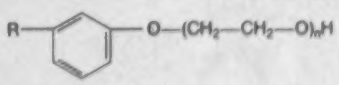
Amine oxides



$R = C_{12-16}$

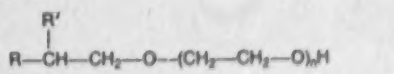
NONIONICS

Alkylphenol ethoxylates



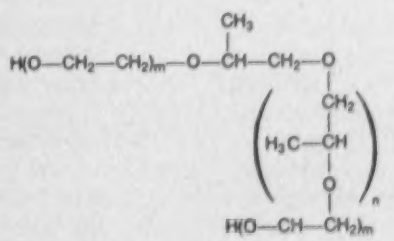
$R = C_{8-12}$
$n = 5-10$

Fatty or oxo-alcohol polyethyleneglycol ethers



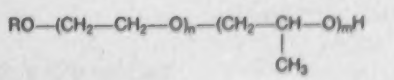
$R = C_{6-15}$
$R' = H, C_1, C_2 \ldots$
$n = 3-15$

Ethylene oxide-propylene oxide polymers



$n = 2-60$
$m = 15-80$

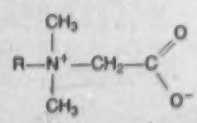
Fatty alcohol polyglycol ethers



$R = C_{8-18}$
$n = 3-6$
$m = 3-6$

AMPHOTERICS

Alkyl betaines (also sulfonated)



$R = C_{12-16}$

tants and many other products. Some of these companies make surfactant materials that are several steps beyond the basic petrochemical.

For example, ethylene producers BASF, Shell Chemical, Texaco Chemical, Union Carbide, and Vista Chemical make first-step intermediates such as ethylene oxide, α-olefins, and various detergent alcohols that subsequently are made into surfactants. These and other companies such as Ethyl and Sherex Chemical either sell the intermediates or further process them into surfactants to be blended into detergents and other products.

The number of surfactants and intermediates for surfactants offered by basic producers continues to grow as consumers search for more specificity in the detergent or other product for the final market, says Jerry G. Moffet Jr., business manager of detergent products at Shell Chemical. For example, he says that Shell offers many more individual items than previously in its product line of ethoxylates. These ethoxylates differ in the numbers of ethylene oxide groups in them, thereby providing different final surface active properties.

A similar viewpoint comes from Walter Whitla, who formerly was manager of marketing for detergent materials with Akzo Chemie America and is now corporate director of purchasing. He says that 50% of 1987 sales volume came from products that the company did not offer three years ago, many of which are the result of the company's R&D programs. Akzo has been particularly pursuing development and sales of various new kinds of fabric softeners and antistatic agents that are blended into household and other detergent formulations as auxiliary materials to surfactants.

The expansion of product lines in surfactant and auxiliary materials, largely through R&D but also through purchase of part or all of other companies, is for many companies a long-term characteristic of the detergent materials industry. The entire industry related to surface active products has long been known to be among the most creative parts of the chemical industry—

and, according to some, among the most creative of all industries. The enormous product lines offered by the 200 or more companies that are part of this business have developed through efforts to find new products to fit old uses in better ways and through finding new uses for old products, some of which may be 100 years old or less than five.

Product line expansions affect companies differently. Some new products can be added by changing plants through relatively minor equipment and processing modifications. Others require new units if the anticipated sales volume is large. For example, BASF is adding a unit at its Spartanburg, S.C., plant to increase its line of acrylic acid-based homopolymers and copolymers, according to Kenneth F. Schoene, director of performance chemicals business at BASF Corp.'s chemical division. Such polymers are used as functional additives such as anti-redeposition and anti-incrustation agents or as processing aids in the manufacture of powder household detergents. The unit is scheduled to begin operating in mid-1988.

Behind expansion of product lines to fit demands for surfactant and other materials are competitive pressures on sellers of the final product, whether it goes into household, industrial, or institutional markets. As a result, formulations are changed and products frequently added or withdrawn.

Factors other than surface active properties or whiteness of clothing after washing strongly influence demand for detergent materials. For example, convenience is a factor currently affecting formulations. Single-use packages are finding growing acceptance, as are liquid detergents. A complete material is the keystone of meeting the convenience demand: a material that not only cleans, but bleaches, softens, and gives a good "hand" or feel to the clothes after drying, while having a good shelf life and smelling nice too. Not to be neglected are material and packaging costs, which account for roughly 55 cents of every dollar from sales of formulated surfactant products, according to a market study done by Business Trends Analysts of Commack, N.Y.

Technical specialists at BASF's Wyandotte lab use Terg-O-Tometer, computerized reflectance, and other measurements to test laundry and other formulations

Despite demand for convenience, low cost, light weight, ease of handling (part of the reason behind the growing acceptance of liquid household detergents), and other requirements in cleaning formulations, the product nevertheless must do its job as well as or better than another or it soon will be left on the supermarket shelf. That situation means concentration on development of surfactant materials themselves, and (to a lesser degree but not insignificantly) emphasis on builders, bleaching agents, brighteners, and other auxiliary materials that can go into the many formulations.

Surfactants began with a form of soap (salts of carboxylic acids) made as long ago as 2500 BC by the Sumerians living in what is now the countries of Iraq and Iran. Since then, most major civilizations have known some kind of soap, made with slowly growing technical competence. Late in the 18th century, according to H. Verbeek of Henkel in West Germany, an understanding of the structure of fats, a method to make soda ash, and a system to bring large quantities of low-cost vegetable oils from the tropics put soapmaking on a broad technical scale. As the 20th century began, some compounds similar to cur-

Surfactants have characteristic properties

Amphipathic structures. Surfactant molecules are made up of groups of opposite solubilities, such as oil-soluble and water-soluble groups.

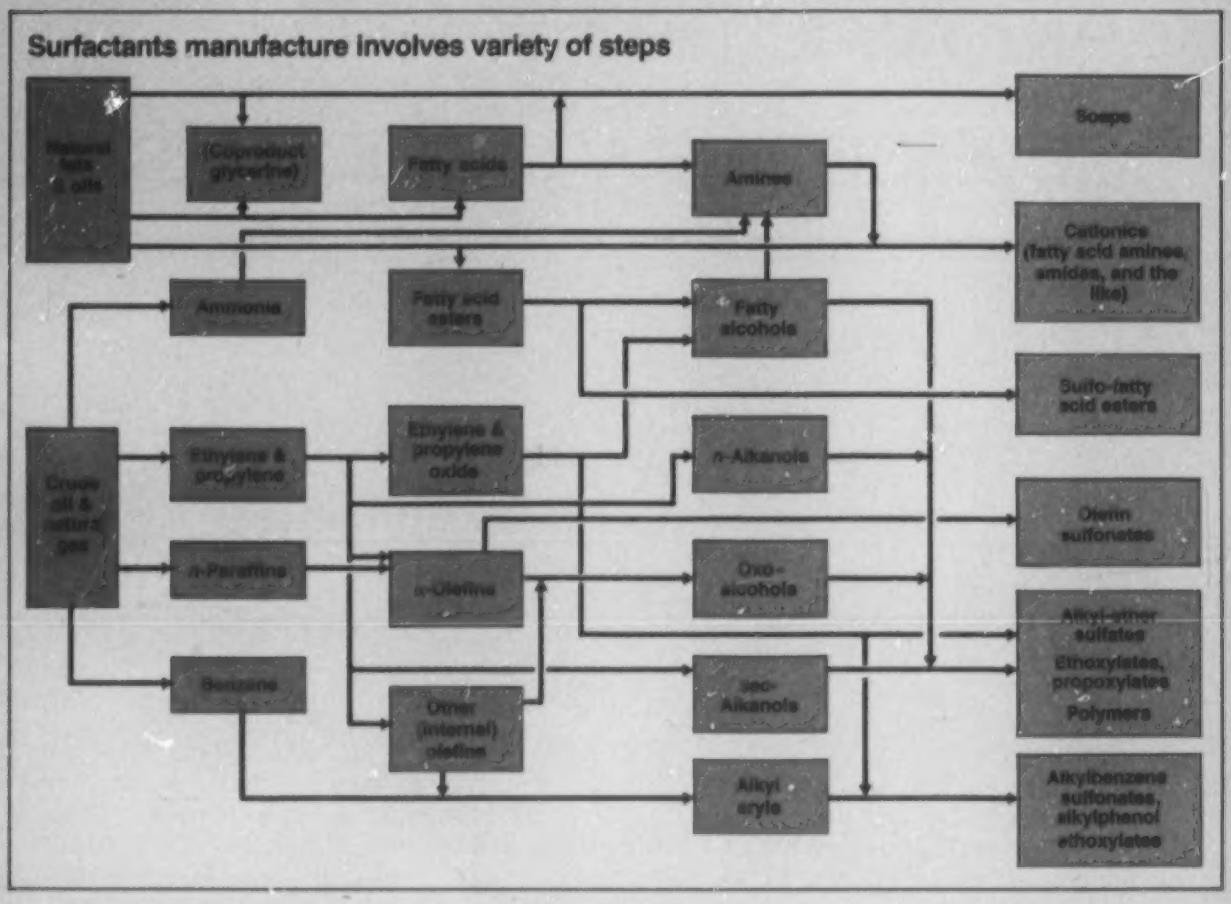
High solubility. Surfactants are highly soluble in at least one phase of a liquid system.

Interfacial adsorption. Surfactant solute at equilibrium is more concentrated at phase interface than in bulk solution.

Interfacial orientation. Surfactant molecules and ions are in oriented monolayers at phase interfaces.

Micelle formation. Surfactants aggregate into micelles or groups of molecules or ions if concentration of surfactant in the bulk solution exceeds a characteristic limiting value, the critical micelle concentration, which is specific for any surfactant-solvent system.

Functional properties. Surfactant solutions have combination of detergency (cleaning), dispersing, emulsifying, foaming, solubilizing, and wetting properties.



rently used surfactants had been made in Germany, but most performed unsatisfactorily as detergents. By the 1930s, a variety of fatty alcohol sulfates were marketed commercially in detergents. Thousands of compounds with amphipathic structures—molecules with groups of opposing solubilities such as an oil-soluble hydrocarbon chain and a water-soluble ionic group—have been made since then.

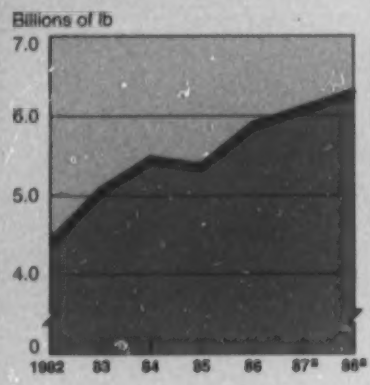
Because of their nature, most soaps are classified as anionic surfactants. Classification depends on the charge on the surface active part of the molecule, usually the larger part. The long hydrocarbon chain derived by splitting tallow and other natural fats or coconut and other natural oils into a hydrocarbon acid and glycerine provides the negative charge. Sodium or another alkali atom provides the positive charge. Most soap commercially made today is sold as the major component of toilet bar soap for personal use and for a host of industrial detergent formulations. In household and other detergents, soap has long been replaced by more effective surfactants, except for specialized uses such as a foam regulator.

Useful production estimates of soaps as formulated are unavailable. Production of carboxylic acids and salts in 1986 totaled about 760 million lb, according to ITC. Sodium salts of tallow acids accounted for slightly less than 370 million lb, or about 50% of the total production of carboxylic acids and salts. These materials were about 10% of the 3.66 billion lb of anionic surfactants produced in 1986. The outlook for growth of soaps is less rosy than for surfactants in general because other surfactants continue to capture some markets from soap and because use of soap depends heavily on the personal care products markets, which have heavy competition from many kinds of cleaning products.

Sulfonic acids and their salts are the dominant part of the anionic surfactant business. Almost 2.1 billion lb of these materials were made in 1986, up 17% from about 1.8 billion lb produced in 1985. Several major groups of products make up the sulfonic acid and salts share of anionic surfactants. Largest is the ligninsulfonates and naphthalenesulfonates group. Next is the group of sulfuric acid esters, closely followed by the alkylbenzenesulfonates.

As their name implies, ligninsulfonates are made from the lignin in wood by the simple reaction of sulfur dioxide and calcium sulfite. In 1986, the production of ammonium, calcium, and sodium salts of ligninsulfonates totaled more than 850 million lb, or more than 90% of the group of lignin- and naphthalenesulfonates. Most are used as inexpensive dispersing agents in industrial applications such as ore flotation and oil well drilling. Whether these products grow depends on those two industries, both of which currently are operating below nor-

Surfactant output to hit 6.3 billion lb this year



a Estimate. Sources: International Trade Commission, C&EN estimates

mal levels. Production of these sulfonates was down in 1986, reflecting that condition. The outlook for 1988 is for a minor increase from the 1986 level of production.

More than 770 million lb of sulfuric acid esters were produced in 1986, according to ITC, most based upon either linear alcohols with chains of 12 to 18 carbons or upon ethoxylated alcohols, which are sulfonated with sulfur trioxide or chlorosulfonic acid. Sources of those alcohols are either natural coconut oil or ethylene polymerization using Ziegler technology. The choice of feedstock to be used for making the alcohols depends on cost of the ethylene (crude oil prices) compared with cost of the coconut oil and the supply situation for coconut oils. Ethoxylation of the alcohols with varying quantities of ethylene oxide produces alcohol ether sulfates.

The alcohol sulfates often have been regarded as the first of the modern synthetic detergents, although they have been used commercially for more than 50 years. If a builder such as sodium tripolyphosphate can be used with them in a detergent formulation, then the performance of the formulation is acceptable for many household laundry detergents. If no phosphates are used, then sulfated alcohol ethyoxylates are combined with the alcohol sulfates to improve the final performance. These kinds of alcohol sulfates contain a wide range of ethylene oxide groups, depending on the kinds of end uses for which they are designed.

More than 80% of the production of the various alcohol sulfates goes into various kinds of household and personal care cleaning products. The actual formulations vary widely because, for example, some are aimed at low-cost laundry products, either powdered or liquid, and others are aimed at hair shampoos and hand dishwashing materials, because such materials are known to have little effect on skin.

A number of other alcohol derivatives are produced in relatively small quantities for specialized uses. Some of the derivatives are available as relatively pure compounds, and others are available as mixtures of several alcohols. The alcohols themselves are produced either from ethylene or from natural oils.

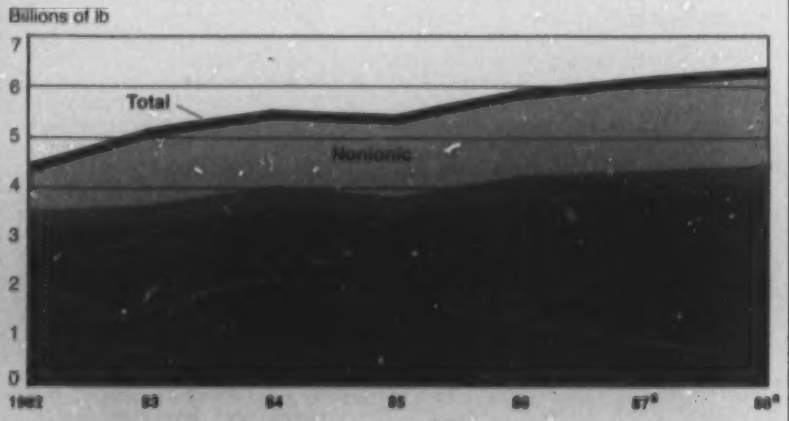
In 1986, more than 750 million lb of linear alkylbenzene sulfonic acids and sulfonates were produced. Three compounds accounted for well over 90% of that total—dodecylbenzenesulfonic acid, and the sodium salts of this acid and of tridecylbenzenesulfonic acid. Reported production of these materials apparently increased greatly during 1986 from 1985 output of less than 570 million lb. However, industry sources suggest that, for some time, reported production has been below actual production, but that improvements in reporting and assembling data now make the reported value closer to the true quantity.

Several large producers and detergent makers produce their own linear alkylbenzene sulfonates (LAS) for captive use; only 20 to 30% of total production is sold on the merchant market. Household laundry and dishwashing products long have dominated LAS use and were the major outlet a number of years ago when the alkyl chain was branched instead of linear. Because biodegradation of branched-chain alkylbenzene sulfonates took so long, these materials caused foaming in wastewater treating plants and in bodies of water receiving them and so are not usually used in household laundry detergent formulations anymore.

Frequent reformulations of household detergents and other products cause some shifting in the kinds and quantities of LAS used. In general, however, production of these kinds of sulfonates has trended downward during the 1980s, as they have been partially replaced by various alcohol sulfates. Outlook for LAS in household and personal care uses appears to be one of slow decline, but is one of slow increase in industrial markets. The net effect will be one of slightly lower output, because industrial uses are only about 25 to 35% of total consumption.

A large number of other compounds with surface active properties fall into the anionic classification. Most are produced in far small-

Output of nonionics growing faster than other types



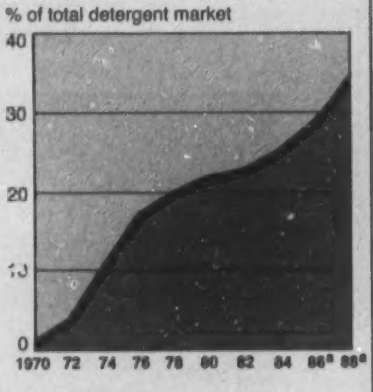
a Estimates (smaller quantities of amphoteric surfactants, less than 30 million lb per year, excluded). Sources: International Trade Commission, C&EN estimates

er quantities than are the three big-volume sulfonic acid salts, and they cost more on a unit basis. Sulfonates of such aromatics as benzene, toluene, cumene, and xylene; dialkyl sulfosuccinates; and numerous phosphate esters are among the larger-volume other products. Most of these compounds have many uses in industry where their cost and various limitations on the conditions under which they are most effective are less important than in the competitive retail markets of household detergents. For example, the phosphoric acid derivatives find use in polymerizations, clothes dry cleaning, textile processing, and pesticide dispersion. Volume growth of this catch-all group of anionic surfactant materials is expected to be spotty. Those anionic surfactants with a special value to a rapidly growing segment of industry will show substantial growth from a relatively small base. As a group, these compounds will grow more slowly than will the alcohol sulfates.

Cationic surfactants, with slightly more than 492 million lb produced in 1986, account for less than 10% of surfactant production, according to ITC. As their name suggests, cationic surfactants have a positive charge on their hydrophobic group. The charge is on the nitrogen atom in an amine or a quaternary ammonium compound. A large number of amines, amine oxides, their salts, and quaternary ammonium salts are produced in small quantities.

Quaternary ammonium salts that do not contain oxygen made up almost one third of cationic surfactant production in 1986. Small quantities of these salts that do contain oxygen also were produced. As a group, quaternary ammonium salts have two distinctly different uses. In household products, they are used as fabric softeners because the positive charge on the quaternary ammonium ion causes strong adsorption on fabrics that generally have a negative charge. This property also makes these compounds useful as antistatic agents in detergent formulations.

Liquid detergents pick up greater share of market



[a] Estimate.
Sources: Shell Chemical, C&EN estimates

Heavy-duty detergents find use in commercial laundries

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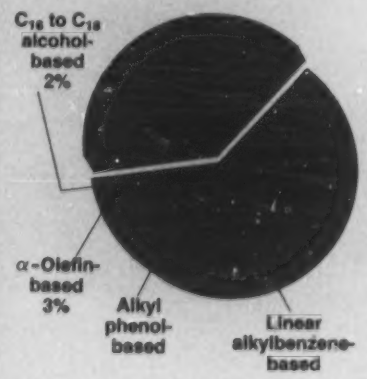
In industrial and institutional uses, quaternary ammonium compounds also find use in ways other than as a surfactant because of some of their germicidal and lubricating properties. Because of their ability to reduce static charge and impart a soft feel to fabrics, quaternary ammonium compounds find most of their industrial uses in textile manufacturing.

The largest volumes of those compounds for which production is reported are based on natural fats and oils such as tallow and coconut oil. Production of quaternary ammonium compounds increased about 10% in 1986 over 1985. The growth in 1987 probably was as good because of various introductions of new derivatives. But growth this year could slow because fewer new products are expected to be introduced.

The other large categories of cationic surfactants are the various amines and amine oxides. More than 100 million lb of amine oxides without amide linkages were produced in 1986. Production of amines without oxygen atoms was almost 150 million lb in 1986. Another 30 million lb of amine and amine oxides with amide linkages also were produced. Growth in production of these amino cationic surfactants was significant in 1986, rising as much as 40% in the case of the group of monoamines.

Soap remains most widely used surfactant



Sources: Shell Chemical, C&EN estimates

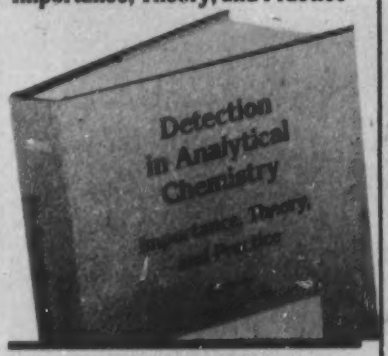
Outlook for production of this group of surfactants depends heavily on the economic conditions that affect industrial production, because the major uses of the amine surfactants are largely in applications such as ore flotation agents, corrosion inhibitors, dispersing agents, wetting agents for asphalt and tar emulsions, and as intermediates in making even more complex derivatives. Amine oxides do go into household products, particularly where additional foam is desired in the washing process, such as in hand dishwashing. They also are used in textile processing, particularly if cotton fibers are involved. Ethoxylated amines find much the same uses in general, but often are specifically tailored for certain uses in the textile industry. Imidazoline derivatives of many kinds also find special application in many of the same uses.

Of the third major type of surfactant, nonionics, more than 1.72 billion lb were produced in 1986, up about 10% from 1985. By far the largest group are the various ethers, produced mainly by ethoxylating alkyl phenols and linear alcohols. These accounted for about 73% of the total. Carboxylic acid esters production totaled 290 million lb, or 17%, and carboxylic amines accounted for less than 10% of production.

The ethers output is dominated by ethoxylated linear alcohols, which accounted for more than 55% of 1986 ethers production. The number of ethylene oxide molecules added to a long-chain alcohol varies widely—possibly by a difference of 50 over the whole line of products—as a result of varying rates of reaction during the ethoxylation process. The broad spectrum of homologs resulting from the ethoxylation reactions roughly follows a Poisson distribution. Depending on their chain length, these ethoxylated alcohols are superior in emulsifying, wetting, and dispersing properties. However, the better surfactant properties result from a relatively few ethylene oxide groups in the molecule. To minimize production of the nonbenzenoid ethers having too few or too many of the groups, considerable catalyst work has been done to keep the distribution as nar-

Detection in Analytical Chemistry

Importance, Theory, and Practice



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Lloyd A. Currie, *Editor*

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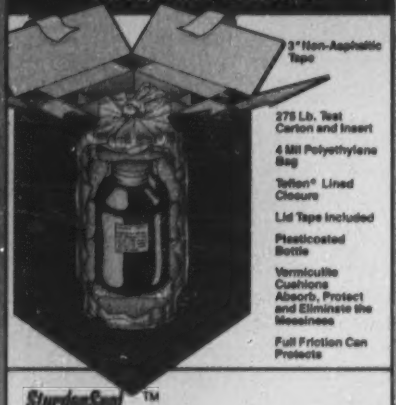
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CIRCLE 11 ON READER SERVICE CARD

Product Report

row as possible around a desired number.

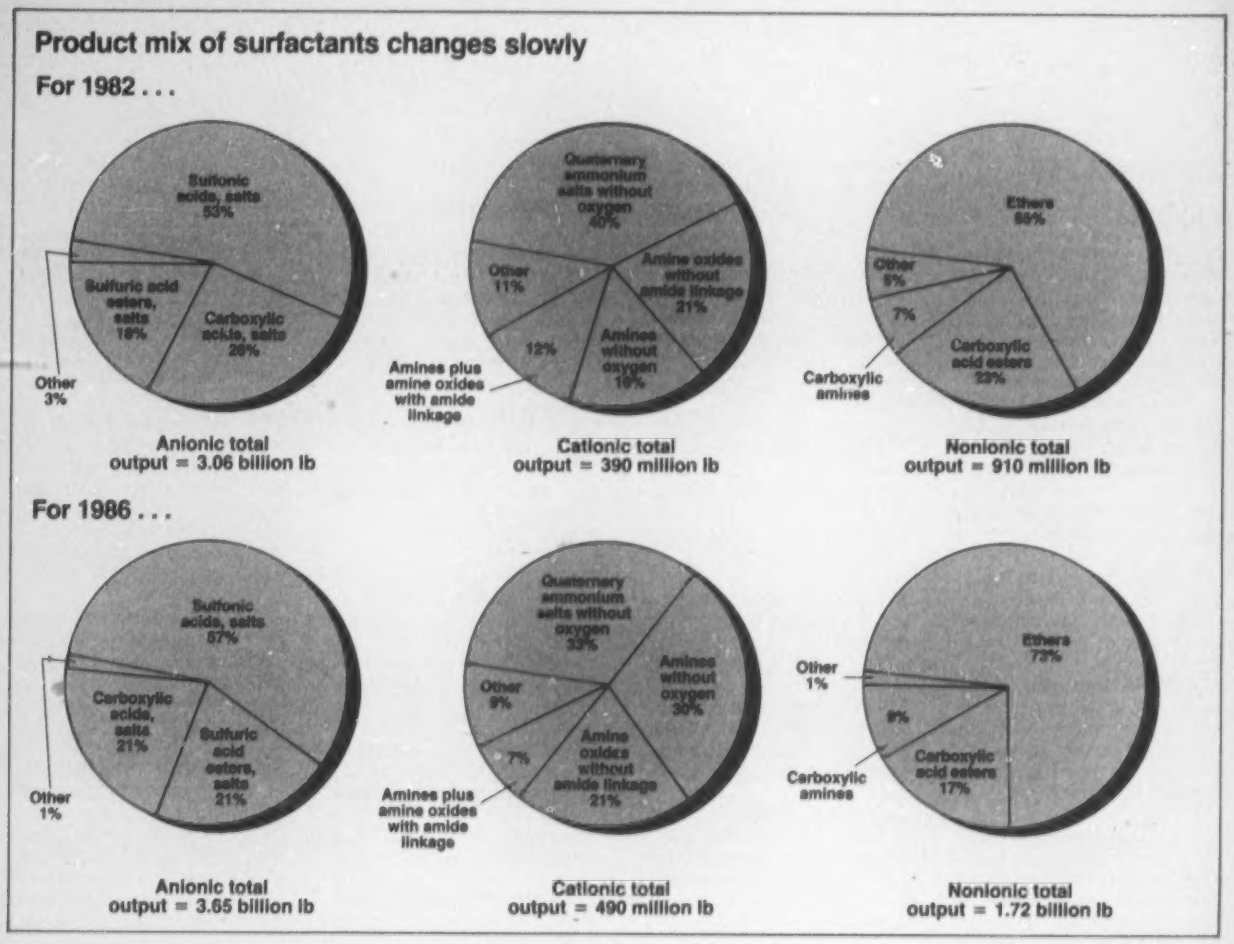
More than three quarters of consumption goes into various household laundry detergents or other household cleaners. The biggest single household use continues to be liquid laundry detergents. Because growth in demand has rekindled for liquid detergents, demand for the alcohol ethoxylates is expected to continue rising at 4 to 6% in 1988, or well above the average growth rate for all surfactants.

A large number of other nonbenzenoid special ethers are made for use as surfactants, but none is produced in the quantities that are produced as mixed ethoxylated linear alcohols. Some of the types of these products are ethoxylated polypropylene glycol, ethoxylated mixed ethylene and propylene glycol, or ethoxylated C_{10} to C_{18} alcohols. Often, they are used in particular industrial applications and are worth the high costs.

Among the benzenoid ethers, ethoxylated nonylphenol dominates. It accounted for more than 75% of 1986 production. Manufacture of these esters follows similar processes and uses equipment similar to that

Surgeon scrubs with specialty soap

Product mix of surfactants changes slowly


For 1982 . . .
Sulfonic acids, salts 53%
Sulfuric acid esters, salts 18%
Carboxylic acids, salts 26%
Other 3%
Anionic total output = 3.06 billion lb
Quaternary ammonium salts without oxygen 40%
Other 11%
Amine oxides without amide linkage 21%
Amines without oxygen 16%
12%
Amines plus amine oxides with amide linkage
Cationic total output = 390 million lb
Ethers 68%
Other 5%
7%
Carboxylic acid esters 23%
Carboxylic amines
Nonionic total output = 910 million lb
For 1986 . . .
Sulfonic acids, salts 57%
Carboxylic acids, salts 21%
Sulfuric acid esters, salts 21%
Other 1%
Anionic total output = 3.65 billion lb
Quaternary ammonium salts without oxygen 33%
Amines without oxygen 30%
Other 9%
7%
Amine oxides without amide linkage 21%
Amines plus amine oxides with amide linkage
Cationic total output = 490 million lb
Ethers 73%
Other 1%
9%
Carboxylic acid esters 17%
Carboxylic amines
Nonionic total output = 1.72 billion lb

used in manufacture of linear alcohol ethoxylates. As a result, several of the producers of these materials also make linear alcohol ethoxylates. The carboxylic esters have marginally better detergency properties but have a problem in slow biodegradability. Consequently, industrial uses predominate and they are expected to continue to do so. Outlook for growth of these esters, therefore, depends on industrial production and on mineral and oil production.

A large number of fatty acids, alcohols, glycols, and glycol polymers are used in the manufacture of esters of carboxylic acids. Various esters of glycerol, of polyethylene glycol, of anhydrosorbitol, and of several natural fats are examples produced in significant quantities. Numerous kinds of these esters are ethoxylated to improve their surfactant properties. Many of the carboxylic acid esters have been approved for use in foods and are widely used as emulsifiers and dispersing agents in bakery products, candies, and dairy products. Others are used in cosmetics and pharmaceuticals. Various industrially used esters are prevalent in such areas as metals fabrication, polymerizations, paint manufacture, and textile processing.

Production of the carboxylic acid ester surfactants in 1986 rose about 12% from 1985 to 290 million lb. In 1987, growth fell to a slightly slower pace of about 10%. A similar rate is expected for 1988, unless the economy slows, with a resultant decline in sales of luxury foods, clothing, and durable goods.

Carboxylic acid amines, with a 1986 reported production total of 153 million lb, are made by reacting fatty acids with hydroxyalkyl amines, mostly diethanolamine. Some of the products are relatively insoluble in water, but they are used in combination with more hydrophilic surfactants. Their uses range from liquid dishwashing detergents to textile processing aids and drycleaning detergents. Growth has been spotty, because individual compounds or limited range groups of compounds vary in demand as the technology of use changes.

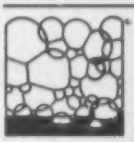
The small quantities of amphoteric surfactants produced in the U.S. are based mostly on derivatives of betaine—trimethyl ammonium acetate. A basic nitrogen group and an acidic carboxyl group are the predominant functional parts of these compounds. High cost limits their use to specialty products, many of which are cosmetics. It is expected that growth of amphoteric surfactants will be slow.

Many other components besides surfactants are used in detergents. In household detergent formulations, for instance, the list of components can be long. These components augment the properties of sur-

factants. Although not universally agreed upon, the component next in importance to the surfactants is the builder. The most important action expected from a detergent builder is to remove metallic ions such as calcium and magnesium, or the "hardness" from the washing fluid. Builders can do this by sequestering these ions (chelating them), precipitating them as insoluble salts, or exchanging them for sodium ions. Builders also can provide alkalinity to the washing media and provide some suspension effect to keep loosened soil particles in the media.

A dozen or more materials are or have been used to some extent as builders in detergent formulations. All have one or more drawbacks that offset their value in the formulations. Sodium tripolyphosphate long has been considered by the industry as the best builder. Its major difficulty comes from its contribution to eutrophication of bodies of water as a result of the fertilization of algae by phosphorus atoms. Now, about 28% of the U.S. has banned phosphate materials from detergent formulations, and those regulations may grow, according to Business Trend Analysts.

Alternatives for sodium tripolyphosphate are widely used by detergent formulators. Compositions and materials change frequently as development work attempts to improve performance of cleaning while offering greater convenience in handling, as well as keeping materials cost as low as possible. One such alternative, sodium citrate, sequesters calcium and magnesium ions much less effectively than does sodium tripolyphosphate. However, it has found growing use because of its high solubility and the increasing demand for liquid laundry detergents. Although cost of sodium citrate has declined significantly, it still is more expensive than sodium tripolyphosphate.



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Zeolites—sodium aluminosilicates—head the list of ion exchangers used in detergent formulations. Most that are used in detergents are of the "Type A" form. This form has the empirical formula, $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5H_2O$, and a particle size in the range of 10 μm. These zeolites handle calcium ions well, but their pore size is too small to absorb hydrated magnesium ions. Being insoluble, their use is limited to powders.

The growth prospects for zeolites may be caught between conflicting actions. If phosphate bans increase, then more zeolites will be used in detergents as builders. But the shift toward liquid detergents will reduce growth of zeolites because of their insolublity. On balance, the outlook for zeolites' demand is expected to be one of slow growth, probably less than overall growth in detergents.

Sodium carbonate and sodium silicate often are combined as builders in detergents. The carbonate causes calcium and magnesium carbonates to precipitate. Unfortunately, despite addition of other materials, the precipitates cannot fully be prevented from redepositing on clothing where it leaves a "hard" feel to the fabric and possibly a grey color resulting from entrapped dirt. Sodium silicate provides alkalinity and buffering in the wash water, as does sodium carbonate. It also gives some corrosion protection for washing machine parts and acts as a processing aid in detergent manufacturing. With the advent of zeolites, use of these materials declined and renewed growth seems to be unlikely in the near term.

Bleaching materials rank another step down in importance in detergent formulations, but they either are a part of the detergent or are a separate addition to the washing program. These materials can be thought of as supplements to the surfactants that aid the physical methods of cleaning. Bleaches containing chlorine have been the standard for many years. Problems of residual chlorine and its odor have shifted some emphasis away from hypochlorites. Addition of dry hypochlorite bleaches to detergents generally is more expensive than is

Shell Oil technicians use automated equipment to test effectiveness of laundry detergents at firm's Westhollow Research Center in Houston

the use of a separate liquid bleach. But in some products, the convenience factor will justify the higher cost.

More recently, the peroxides (usually sodium perborate) have rapidly increased in demand from a relatively small base as a part of attempts by formulators of detergents to provide the convenience of single addition to the wash water. Hydrolysis of the perborate produces hydrogen peroxide, which does the oxidation. An activator frequently is added to the formulation to give good bleaching at low temperatures.

In the 1950s, peroxy carboxylic acids showed high bleaching performance. One of the best performers today is diperoxydodecanedioic acid, but its manufacture on a commercial scale was delayed by safety problems until Degussa and Henkel found a way in situ to desensitize the process. This material meets the requirements of good performance at low wash water temperatures.

The last category of detergent components is the auxiliary materials, the many examples of which are varied in both their composition and uses. Some are surfactants applied in specialized ways to act as antifoamers, fabric softeners, or antistatic agents. Other auxiliaries added to detergents are enzymes aimed at removing proteinaceous material, antiredeposition agents, optical brighteners, perfumes, dyes, filler, and formulation aids. If compared with the quantities of surfactants consumed, the quantities of these materials, except fillers, are tiny. However, most premium-quality detergent formulations for household use now contain most of these auxiliaries.

Enzymes were used in many U.S. formulations in the 1950s and 1960s, but were dropped for cost and performance reasons. Now, with the improvements in enzymes and in the ways of incorporating them in detergents, their use is increasing. Most enzymes have to work relatively rapidly to break a peptide or ester bond to be effective in removing proteinaceous stains.

Optical brighteners are members of several basic organic compound groups that have the ability to convert ultraviolet light into visible blue light. In effect, these materials do the same job that "bluing" agents (mostly ultramarine blue dyes) have been doing since the mid-19th century. Stilbene derivatives account for a large share of the commercially used optical brighteners, although many other compounds such as coumarin, pyrazoline, and quinolone derivatives are used.

Still more auxiliaries may be added to detergent formulations as a result of R&D efforts to provide more convenience and performance. Such additional materials and better surfactants will be needed if sellers are to gain share in the mature and nearly saturated market of detergents. □

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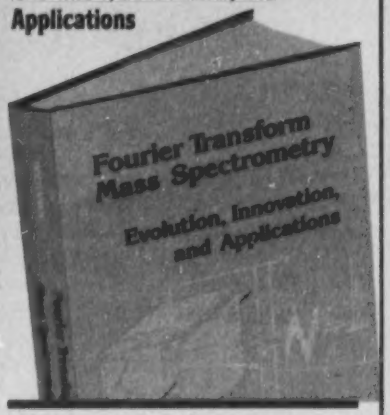

Fourier Transform Mass Spectrometry (FTMS) is a rapidly growing technique that has the potential to become a valuable and versatile tool for both analytical and research applications. This new book brings together researchers who are investigating new applications of FTMS, as well as those who are developing instrumental advances in FTMS. You'll read reports on the current analytical capabilities of FTMS and projections on the future capabilities of this technique. You'll learn about a wide variety of applications, ranging from basic studies of dissociation of ions to the analysis of high molecular weight biopolymers. Topic highlights include:

- Principles and Features of FTMS
- New Excitation and Detection Techniques
- Dual-Cell Fourier Transform Mass Spectrometer
- Instrumentation and Application in Analytical FTMS
- FTMS of Large Biomolecules
- Tandem FTMS of Large Molecules
- Laser Desorption-FTMS
- IR Multiphoton Dissociation of Laser-Desorbed Ions
- Photodissociation of Transition Metal Ions
- Negative Ion Processes

Fourier Transform Mass Spectrometry offers an excellent general introduction to the technique as well as a summary of current applications. This book will be of value to chemists, biologists, physicists, and others interested in learning more about FTMS.

Michelle V. Buchanan, *Editor, Oak Ridge National Laboratory*

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